Chapter 6: Pseudopotential

1. Orthogonalized plane wave
2. Norm-conserving
3. Ultrasoft PP
4. Projection augmented wave

Orthogonalized plane waves

Basis functions for valence states

$$\chi_{\mathbf{q}}^{OPW}(\mathbf{r}) = \frac{1}{\Omega}\left[e^{i\mathbf{q}\cdot\mathbf{r}} - \sum_j \langle u_j | \mathbf{q} \rangle u_j(\mathbf{r}) \right]$$

Herring, 1940

$$\frac{1}{2}\nabla^2 u_j + (E_j - V_j) u_j = 0$$

Optimized potential

Localized functions

Generalized form

$$\psi_{lm}^{v}(\mathbf{r}) = \tilde{\psi}_{lm}^{v}(\mathbf{r}) + \sum_j B_{lmj} u_{lmj}(\mathbf{r})$$

$$B_{lmj} = \int d\mathbf{q}\, c_{lm}(\mathbf{q}) \langle u_j | \mathbf{q} \rangle$$

$$\psi_{lm}^{v}(\mathbf{r}) = \int d\mathbf{q}\, c_{lm}(\mathbf{q}) \chi_{\mathbf{q}}^{OPW}(\mathbf{r})$$

$$\tilde{\psi}_{lm}^{v}(\mathbf{r}) = \int d\mathbf{q}\, c_{lm}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}}$$

Mapping

$$\left| \psi_{lm}^{v} \right\rangle = F \left| \tilde{\psi}_{lm}^{v} \right\rangle$$

Localized functions:

$$u_{lmj} = \psi_{lmj}^{c} \qquad H\psi_{lmj}^{c} = \varepsilon_{lj}^{c} \psi_{lmj}^{c}$$

$$\left\langle \chi_{\mathbf{q}}^{OPW} \middle| \chi_{\mathbf{q}}^{OPW} \right\rangle = 1 - \sum_j \left| \langle u_j | \mathbf{q} \rangle \right|^2$$

NOT orthogonal!

Nonlocal operator

PKA transformation

Phillips, Kleinman, and Antoncik, 1954,1959

$$\hat{H}\psi_i^v(\mathbf{r})=\left[-\frac{1}{2}\nabla^2+V(\mathbf{r})\right]\psi_i^v(\mathbf{r})=\varepsilon_i^v\psi_i^v(\mathbf{r})$$

For smooth function

$$\hat{H}^{PKA}\tilde{\psi}_i^v(\mathbf{r})=\left[-\frac{1}{2}\nabla^2+\hat{V}^{PKA}\right]\tilde{\psi}_i^v(\mathbf{r})=\varepsilon_i^v\tilde{\psi}_i^v(\mathbf{r})$$

Generalized eigenvalue problem

$$\hat{V}^{PKA}=V+\hat{V}^R \qquad \hat{V}^{PKA}\tilde{\psi}_i^v(\mathbf{r})=\sum_j\left(\varepsilon_i^v-\varepsilon_j^c\right)\left\langle\psi_j^c\middle|\tilde{\psi}_i^v\right\rangle\psi_j^c(\mathbf{r})$$

Semi-local form

Nonlocal potential

$$\hat{V}_{SL}=\sum_{lm}\left|Y_{lm}\right\rangle V_l(r)\left\langle Y_{lm}\right|$$

Nonlocal in angular but local in radial

$$\left[\hat{V}_{SL}f\right]_{r,\theta,\varphi}=\sum_{lm}Y_{lm}(\theta,\varphi)V_l(r)\int d(\cos\theta')d\varphi' Y_{lm}(\theta',\varphi')f(r,\theta',\varphi')$$

$$\left\langle\psi_i\middle|\hat{V}_{SL}\middle|\psi_j\right\rangle=\int dr\,\psi_i(r,\theta,\varphi)\left[\hat{V}_{SL}\psi_j\right]_{r,\theta,\varphi}$$

Norm-conserving PP

Two ways to generate potentials:

1. Empirical
2. Ab initio

Fitted to experiment

Calculations on atoms

Orthonormality conditions:

$$\left\langle \psi_i^{\sigma,PS} \middle| \psi_j^{\sigma',PS} \right\rangle = \delta_{i,j}\delta_{\sigma,\sigma'} \qquad \left(H_{KS}^{\sigma,PS} - \varepsilon_i^{\sigma}\right)\psi_i^{\sigma,PS}(\mathbf{r}) = 0$$

Norm-conserving condition:

1. Atomic reference configuration
2. Beyond a chosen core radius R_c
3. Logarithmic derivatives of WFs agree at R_c
4. Integrated charge inside R_c agrees
5. First energy derivative of the LDs of WFs agrees at R_c and for all r> R_c

Atomic potential outside the cutoff

Logarithmic derivative D:

$$D_l(\varepsilon,r) \equiv r\psi_l'(\varepsilon,r)/\psi_l(\varepsilon,r) = r\frac{d}{dr}\ln\psi_l(\varepsilon,r)$$

Norm-conservation:

$$Q_l = \int_0^{R_c} drr^2\left|\psi_l(r)\right|^2 = \int_0^{R_c} dr\left|\phi_l(r)\right|^2$$

Norm-conservation

Radial equation for a spherical system

$$-\frac{1}{2}\phi_l''(r)+\left[\frac{l(l+1)}{2r^2}+V_{eff}(r)-\varepsilon\right]\phi_l(r)=0$$

$$\Downarrow$$

$$x_l(\varepsilon,r)\equiv\frac{d}{dr}\ln\phi_l(r)=\frac{1}{r}[D_l(\varepsilon,r)+1]$$

$$x_l'(\varepsilon,r)+[x_l(\varepsilon,r)]^2=\frac{l(l+1)}{r^2}+2[V_{eff}(r)-\varepsilon]$$

First energy derivative is obtained by:

$$\frac{\partial}{\partial\varepsilon}x_l'(\varepsilon,r)+2x_l(\varepsilon,r)\frac{\partial}{\partial\varepsilon}x_l(\varepsilon,r)=-1$$

$$\Downarrow$$

$$f'(r)+2x_l(\varepsilon,r)f(r)=\frac{1}{\phi_l(r)^2}\frac{\partial}{\partial r}[\phi_l(r)f(r)]$$

At radius R:

$$\frac{\partial}{\partial\varepsilon}x_l(\varepsilon,R)=-\frac{1}{\phi_l(R)^2}\int_0^R dr\,\phi_l(r)^2=-\frac{1}{\phi_l(R)^2}Q_l(R)$$

Condition 5 satisfied!

Dimensionless logarithmic derivative:

$$\frac{\partial}{\partial\varepsilon}D_l(\varepsilon,R)=-\frac{R}{\phi_l(R)^2}\int_0^R dr\,\phi_l(r)^2=-\frac{R}{\phi_l(R)^2}Q_l(R)$$

Ultrasoft PP

Smooth function (not norm conserving):

Blöch and Vanderbilt, 1990

$$\tilde{\phi} = r\tilde{\psi}$$

$\phi = r\psi$ Norm-conserving

Norm difference:

$$\Delta Q_{s,s'} = \int_0^{R_c} dr \Delta Q_{s,s'}(r)$$

$$\Delta Q_{s,s'}(r) = \phi_s^*(r)\phi_{s'}(r) - \tilde{\phi}_s^*(r)\tilde{\phi}_{s'}(r)$$

Auxiliary function

Define a new nonlocal potential operator

$$\delta\hat{V}_{NL}^{US} = \sum_{s,s'} D_{s,s'} |\beta_s\rangle\langle\beta_{s'}|$$

where

$$D_{s,s'} = B_{s,s'} + \varepsilon_{s'}\Delta Q_{s,s'}$$

Generalized eigenvalue problem

$$\left[\hat{H} - \varepsilon_s \hat{S}\right]\tilde{\psi}_s = 0$$

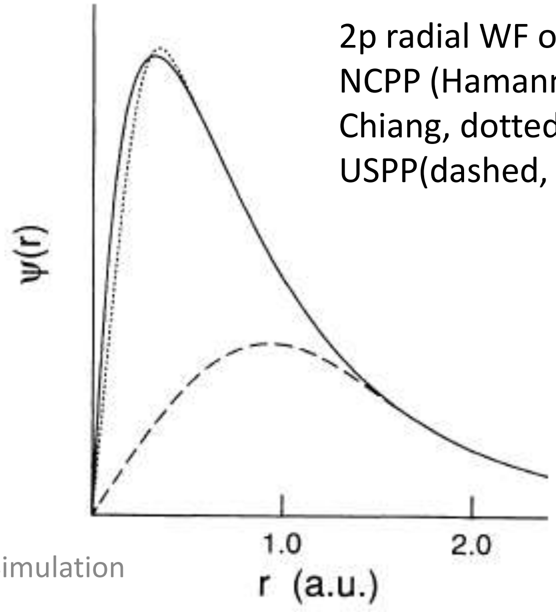
with

$$\hat{H} = -\frac{1}{2}\nabla^2 + V_{local} + \delta\hat{V}_{NL}^{US}$$

$$\hat{S} = \hat{\mathbf{1}} + \sum_{s,s'} \Delta Q_{s,s'} |\beta_s\rangle\langle\beta_{s'}|$$

Norm-conserving:

$$\Delta Q_{s,s'} = 0$$



2p radial WF of oxygen (solid), NCPP (Hamann-Schluter-Chiang, dotted), and USPP(dashed, PRB 1990)

Ultrasoft PP

Solving generalized eigenvalue problem

$$\langle \tilde{\psi}_i | \hat{S} | \tilde{\psi}_j \rangle = \delta_{ij}$$

Normalization condition:

Valence density:

$$n_v(\mathbf{r}) = \sum_{n,\mathbf{k}}^{occ} \tilde{\psi}^*_{n\mathbf{k}}(\mathbf{r})\tilde{\psi}_{n\mathbf{k}}(\mathbf{r}) + \sum_{i,j} \rho_{ij} \Delta Q_{ji}(\mathbf{r}) \qquad \text{with} \qquad \rho_{ij} = \sum_{n,\mathbf{k}}^{occ} \langle \beta_i | \tilde{\psi}_{n\mathbf{k}} \rangle \langle \tilde{\psi}_{n\mathbf{k}} | \beta_j \rangle$$

Variational theory:

$$E_{total} = \sum_{n,\mathbf{k}}^{occ} \left\langle \psi_{n,\mathbf{k}} \middle| \left(-\frac{1}{2}\nabla^2 + V_{loc}^{ion} + \sum_{i,j} D_{ij}^{ion} | \beta_i \rangle \langle \beta_j | \right) \middle| \psi_{n,\mathbf{k}} \right\rangle + E_{Hartree}[n_v] + E_{II} + E_{xc}[n_v]$$

Unscreened bare ion PP

Minimize the functional subject to the constraint of the normalization

$$V_{local}^{ion} \equiv V_{local} - V_{Hxc}$$

$$V_{Hxc} = V_H + V_{xc}$$

$$D_{ij}^{ion} \equiv D_{ij} - D_{ij}^{Hxc}$$

$$D_{ij}^{Hxc} = \int d\mathbf{r} V_{Hxc}(\mathbf{r}) \Delta Q_{ij}(\mathbf{r})$$

Generalized eigenvalue problem:

$$\left(-\frac{1}{2}\nabla^2 + V_{local} + \delta\hat{V}_{NL}^{US} - \varepsilon_{n\mathbf{k}} \hat{S} \right) | \tilde{\psi}_{n\mathbf{k}} \rangle = 0$$

Solved by iterative methods

PAW

Projector augmented waves

Blöch, 1994

all-electron WF

$$\left|\psi_{lm}^{v}\right\rangle = F\left|\tilde{\psi}_{lm}^{v}\right\rangle$$

Smooth WF

Keep all-electron WF

Linear transformation

Expand the smooth function in partial waves

$$\left|\tilde{\psi}\right\rangle = \sum_m c_m \left|\tilde{\psi}_m\right\rangle$$

correspondingly

$$\left|\psi\right\rangle = F\left|\tilde{\psi}\right\rangle = \sum_m c_m \left|\psi_m\right\rangle$$

The full WF

$$\left|\psi\right\rangle = \left|\tilde{\psi}\right\rangle + \sum_m c_m \left(\left|\psi_m\right\rangle - \left|\tilde{\psi}_m\right\rangle\right)$$

Projection operator

$$c_m = \left\langle \tilde{p}_m \middle| \tilde{\psi} \right\rangle$$

$$\left\langle \tilde{p}_m \middle| \tilde{\psi}_{m'} \right\rangle = \delta_{mm'}$$

$$F = 1 + \sum_m \left(\left|\psi_m\right\rangle - \left|\tilde{\psi}_m\right\rangle\right)\left\langle \tilde{p}_m\right|$$

PAW transformation operator

$$\Rightarrow \quad \left|\tilde{\psi}\right\rangle = \sum_m \left|\tilde{\psi}_m\right\rangle\left\langle \tilde{p}_m \middle| \tilde{\psi}\right\rangle$$

The transform of any operator is given by:

$$\tilde{A} = F^{+}\hat{A}F = \hat{A} + \sum_{mm'} \left|\tilde{p}_m\right\rangle\left(\left\langle \psi_m \middle| \hat{A} \middle| \psi_{m'}\right\rangle - \left\langle \tilde{\psi}_m \middle| \hat{A} \middle| \tilde{\psi}_{m'}\right\rangle\right)\left\langle \tilde{p}_{m'}\right|$$

PAW

The density

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + n^1(\mathbf{r}) - \tilde{n}^1(\mathbf{r})$$

Full density

$$\tilde{n}(\mathbf{r}) = \sum_i f_i |\tilde{\psi}_i(\mathbf{r})|^2$$

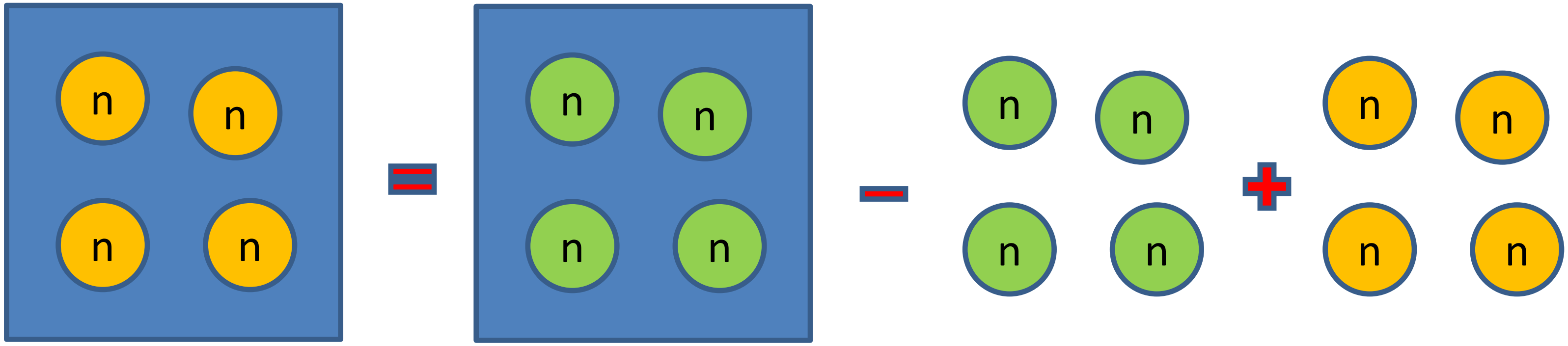
Smooth function

$$n^1(\mathbf{r}) = \sum_i f_i \sum_{mm'} \langle \tilde{\psi}_i | \tilde{\psi}_m \rangle \psi^*_m(\mathbf{r}) \psi_{m'}(\mathbf{r}) \langle \tilde{\psi}_{m'} | \tilde{\psi}_i \rangle$$

Full density inside sphere

$$\tilde{n}^1(\mathbf{r}) = \sum_i f_i \sum_{mm'} \langle \tilde{\psi}_i | \tilde{\psi}_m \rangle \tilde{\psi}^*_m(\mathbf{r}) \tilde{\psi}_{m'}(\mathbf{r}) \langle \tilde{\psi}_{m'} | \tilde{\psi}_i \rangle$$

Smooth function inside sphere



Scattering problem

One electron Schrodinger equation

$$\hat{H}\psi(r)=E\psi(r)$$

with

$$\hat{H}=-\frac{\hbar^2}{2m}\nabla^2+\hat{V}_{ext}(r)$$

Spherical coordinates:

$$\nabla^2=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

Radial WF

$$-\frac{1}{2r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi_{n,l}\right)+\left[\frac{l(l+1)}{2r^2}+V_{ext}(r)-\varepsilon_{n,l}\right]\psi_{n,l}(r)=0$$

$$\Big\downarrow$$

$$-\frac{1}{2}\frac{d^2}{dr^2}\phi_{n,l}(r)+\left[\frac{l(l+1)}{2r^2}+V_{ext}(r)-\varepsilon_{n,l}\right]\phi_{n,l}(r)=0$$

The solution

$$\psi_{nlm}(r)=\psi_{nl}(r)Y_{lm}(\theta,\varphi)=\frac{\phi_{nl}(r)}{r}Y_{lm}(\theta,\varphi)$$

$$Y_{lm}(\theta,\varphi)=\sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m[\cos\theta]e^{im\varphi}$$

Plane wave in spherical function

$$e^{i\mathbf{q}\cdot\mathbf{r}}=4\pi\sum_L i^l j_l(qr)Y_L^*(\hat{\mathbf{q}})Y_L(\hat{\mathbf{r}})$$

Φ independent

$$e^{iqr\cos\theta}=\sum_l(2l+1)i^l j_l(qr)P_l[\cos\theta]$$

Phase shift

Plane wave expansion in spherical function

$$Y_L(\vec{\mathbf{r}})=i^l\psi_{nl}(r)Y_{lm}(\theta,\varphi)=i^l\frac{\phi_{nl}(r)}{r}Y_{lm}(\theta,\varphi)$$

The solution in large r region

Phase shift

$$\psi_l^>(\varepsilon,r)=C_l\left[j_l(\kappa r)-\tan[\eta_l(\varepsilon)]n_l(\kappa r)\right]$$

regular irregular

$$\kappa^2=\varepsilon$$

To determine the phase shift

$$D_l(\varepsilon,r)\equiv r\psi_l'(\varepsilon,r)/\psi_l(\varepsilon,r)=r\frac{d}{dr}\ln\psi_l(\varepsilon,r)$$

$$\psi_l^>(\varepsilon,s)=\psi_l(\varepsilon,s)$$

$$\frac{d}{dr}\psi_l^>(\varepsilon,s)\Big|_s=\frac{d}{dr}\psi_l(\varepsilon,s)\Big|_s$$

$$\tan[\eta_l(\varepsilon)]=\frac{s\frac{d}{dr}j_l(\kappa r)\Big|_s-D_l(\varepsilon,s)j_l(\kappa s)}{s\frac{d}{dr}n_l(\kappa r)\Big|_s-D_l(\varepsilon,s)n_l(\kappa s)}$$

For $\varepsilon=\frac{1}{2}k^2>0$

$$\psi_l^>(\varepsilon,r)\rightarrow\frac{C_l}{kr}\sin\left[kr+\eta_l(\varepsilon)-\frac{l\pi}{2}\right]$$

Full scattering function:

$$\psi_l^>(\varepsilon,r)\rightarrow e^{i\mathbf{q}\cdot\mathbf{r}}+i\frac{e^{iqr}}{qr}\sum_l(2l+1)e^{i\eta_l}\sin(\eta_l)P_l(\cos\theta)$$

Homework

Due: April 26, 2016

To do：**Evaluation on the accuracy and efficiency of plane wave methods.**

选取如下任意两种不同方法，查阅相关文献，比较该两种方法对于某一材料体系的理论计算结果，以及理论结果与实验值的差异（精度）；比较该两种方法计算量，即所需要的运算时间（效率，比如完成一次总能计算所需要的时间）。

可选取的方法：

- OPW
- PAW
- USPP
- NCPP
- APW
- KKR
- FLAPW
- LAPW
- FPLMTO
- MTO
- LMTO
- NMTO

可选取的体系：例如（但不限于）Al，C，Si，Ge，bcc Fe，CaF_2，GaAs 等

比较的内容：例如（但不限于）晶体结构晶胞参数，能带结构等